

Intensification of Natural Gas Conversion to the Key Products of Petrochemical Synthesis and Engine Fuels

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Abstract—An analysis of technologies for producing engine fuels from natural gas is performed. Their main advantages and disadvantages are determined. A technology without feedstock recirculation for producing environmentally clean high-octane engine fuels and the key products of petrochemical synthesis (lower olefinic hydrocarbons, dimethyl ether, and methanol) is proposed. On the basis of laboratory and bench tests of the new process, mathematical models of a catalyst grain and catalytic reactors and the kinetic models of the reactions of the production of synthesis gas, methanol, dimethyl ether, olefins, and the components of engine fuels are constructed and their parameters are estimated. It is shown that the models are in agreement with experimental data. An energy and resource-saving scheme for producing engine fuels that ensures a decrease in the prime cost of the target products is calculated.

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INTRODUCTION

In connection with the decrease in the reserves of raw hydrocarbon materials (petroleum, gas condensate, and natural gas) and the stable increase in their prices, of great importance is the problem of the development of high-efficiency processes for the conversion of hydrocarbons with low feedstock and energy consumption. There are different ways for solving this problem: first, by developing new catalysts that ensure a sharp decrease in the number and quantity of byproducts and power consumption along with an increase in the production rate of a process and, second, by developing new types of catalytic reactors, mass transfer apparatuses, and energy equipment that favor a considerable decrease in the prime cost of manufactured products owing to a reduction in the capital intensity of productions and operating costs. However, the implementation of such measures in practice leads to considerable starting financial expenses and considerable periods of their payback. Therefore, other ways that can be implemented both in operating plants and in factories being designed and that lead to a rapid return of funds invested in production are preferable.

At present, of particular importance is the conversion of natural hydrocarbons to the key products of chemical and petrochemical syntheses that are of a high quality and to environmentally clean high-octane engine fuels. Under conditions of a steady increase of environmental pollution, requirements regarding the quality of engine fuels also increase. The octane numbers of engine fuels should not be lower than 95–98, and the content of harmful impurities (sulfur and nitrogen-containing compounds) should not be higher than several hundred ppm. The production of hydrocarbon engine fuels with such characteristics from conven-

tional petroleum and gas condensates is technologically difficult, and the prime cost of such products will be rather high.

The solving of the above problem using natural gas extracted in Russia is much easier, and the quality of gasolines produced from natural gas is extremely high and meets all of the requirements of the world standards not only at present, but also in the near future over the next 10–20 years.

To reduce the prime cost of the engine fuels produced from natural gas, it is necessary, first, to further improve the technology for natural gas conversion into hydrocarbon engine fuels and, second, to place setups and plants for natural gas conversion closer to extraction sites.

To the present time, some large gas fields have entered the stage of decreasing production. Around them, many large settlements with a population ranging from a thousand to tens of thousands of people are built and equipped. The conversion of natural gas from low-pressure fields to engine fuels and the key products of chemical and petrochemical synthesis directly in the field turns out to be promising, since the infrastructure of settlements and cities is retained and the population gets well-paid work for 40–70 years, and, at the same time, an environmentally clean high-octane engine fuel that satisfies European standards is produced.

The price of natural gas from fields with a low formation pressure is substantially lower than the price of natural gas from fields with a high formation pressure, since the transportation of the former through long-distance pipelines is not profitable. From here, there arises a problem of the effective use of low-pressure natural gas. Its conversion

to carburetor engine fuels and diesel fuels of various grades is undoubtedly promising and profitable. The production of fuels in the places of direct extraction of natural gas is cost effective, since there is no necessity for the delivery of fuel from the industrial regions of the Russian Federation to northern regions, which leads to a sharp increase in its price.

However, the development of a wide network of commercial plants and factories for gas conversion in the Russian Federation will be successful only if engine fuels and the key products of chemical and petrochemical syntheses produced from gas are cheaper than fuels produced from petroleum.

One of the promising processes of the production of engine fuels is the Mobil process, which consists of several stages: 1) the conversion of natural gas into synthesis gas, 2) the conversion of synthesis gas into methanol, 3) the conversion of methanol into dimethyl ether (DME), and 4) the conversion of the mixtures of methanol and DME into hydrocarbons of engine fuels.

This scheme of production with a total capacity of 570 thousand t/yr was implemented in New Zealand in 1985 [1]; however, a sharp decrease in the prime cost of engine fuels was not achieved, in particular, due to the following causes: 1) the prime cost of the produced synthesis gas turned out to be rather high due to the use of the process of the steam conversion of natural gas, and 40% of it is not used efficiently, since it is spent on heating the feedstock to the reaction temperature; 2) the prime cost of the produced methanol is also rather high, since a recirculation technology of methanol production is used in which the volumetric flow rate of the unreacted synthesis gas that is recycled is an order of magnitude higher than the volumetric flow rate of the fresh synthesis gas that is supplied to a reactor for methanol synthesis; and 3) the produced engine fuels contain a considerable (up to 40–60 wt %) amount of aromatic hydrocarbons, whereas for the Euro-3 and Euro-4 fuels their content should not exceed 20 wt % at octane numbers of 93–98.

Therefore, due to a sharp decrease in the prices of petroleum in 1985–1990, the price of produced gasoline exceeded the world prices for gasoline. The operation of the plant became unprofitable and it was rearranged for methanol production.

Under the conditions of new prices for raw hydrocarbon materials and energy, a technology for producing fuels according to the Mobil scheme can be highly effective, especially in its versions where the prime cost of the obtained intermediate products (synthesis gas, methanol, and DME) decreases by 10–15% and the range of produced gasolines increases, first of all, due to an increase in the isoctane hydrocarbons that are present in them.

In the Russian Federation, which is the largest gas-producing state in the world, an additional requirement on the technologies being developed is imposed: they should be applied with a large effect both to stationary large-capacity plants and to modular setups with small and medium capacities that operate directly in the places of the extrac-

tion of natural gas and gas condensate. At the same time, the designs of individual apparatuses should allow for their operation in the Far North and the manufacture should be possible both in the RF and in other countries.

There are different solutions of the above problem.

The first solution is to develop new complex catalysts that make it possible to carry out combined catalytic processes in a reactor. In other words, it is necessary to organize a structured complex of reactions in certain catalytic zones in which each individual reaction occurs under conditions that are optimum for this reaction. This makes it possible to ensure the following: a high efficiency of the process at a given selectivity; the combination of exo- and endothermic reactions in individual catalytic reaction zones, which leads to a sharp decrease in energy consumption; and the combination of certain sets of reactions in individual catalytic reaction zones that make it possible to obtain target products of a high quality, in particular, engine fuels with close octane characteristics and various hydrocarbon compositions. The variation of the latter ensures various ecological indices of the operation of an engine in terms of harmful emissions into the environment.

S.Z. Roginskii, Corresponding Member of the USSR Academy of Sciences, defined such an approach to the organization of a catalytic process in the 1960s–1970s as the “cybernetics of a chemical process” [2]. It can easily be seen that this approach is also almost always implemented in animate nature. The overwhelming majority of chemical engineering processes occur in it without large pressures and temperatures.

The second solution is to organize combined physico-chemical reactive mass transfer and reactive heat transfer processes that are carried out both in a single apparatus and in a set of apparatuses of various designs. The integration of a catalytic process with the physical processes of mass, heat, and energy transfer makes it possible to remove the thermodynamic limitations in conducting the process. High degrees of the conversion of reactants and high characteristics of the process in terms of production rate, selectivity, and energy saving turn out to be attainable.

With the use and development of the above approaches, theoretical and experimental studies were conducted in order to improve the main stages of the process of the production of engine fuels from natural gas for the purpose of decreasing the prime cost of the produced synthesis gas, methanol, DME, and hydrocarbons of engine fuels. At the first stage of research, an experimental study of the statics and dynamics of the process of synthesis gas production from natural gas using nickel catalysts and the modeling of the process using the constructed models for the purpose of its intensification were carried out. Along with the intensification of the process, it was also intended to solve the following problems: decreasing the consumption norms for carbon and power, reducing the prime cost of the target product, and ensuring the specified composition of the target product.

MODELING OF THE PROCESS OF SYNTHESIS GAS PRODUCTION FROM NATURAL GAS

The modeling of the process of the production of synthesis gas was carried out according to the following stages: 1) performing a kinetic experiment and an analysis of its results, 2) construction of a kinetic model of the reaction of the steam–oxygen reforming of methane and the estimation of kinetic constants, 3) analysis and modeling of the process in the grain of a catalyst, and 4) construction of a model of a catalytic autothermal reactor and the choice of the design of the reactor and the modes of its operation.

Kinetic model of the reaction of the steam–oxygen of methane. A complete kinetic model was constructed for the 11-stage mechanism of the reaction of the partial oxidation of methane that includes three slow stages 2, 5, and 9 and eight rapid quasi-equilibrium stages 1, 3, 4, 6, 7, 8, 10, and 11.

The kinetic model of the reaction of the partial oxidation of methane in the presence of water and carbon dioxide in the feedstock is written as

$$R_1^B = -0.5(-W_2 + W_5 + W_9), \quad (1)$$

$$R_2^B = W_2 + 2W_5, \quad (2)$$

$$R_3^B = -W_5, \quad (3)$$

$$\begin{aligned} W_2 &= k_{+2}X_6X_7^3 - k_{-2}X_8X_9^2 \\ &= (k_{+2}X_6 - k_{-2}(K_{(1)})^{-0.5}K_{(3)})X_1^{0.5}X_2, \end{aligned} \quad (4)$$

$$\begin{aligned} W_5 &= ((k_{+5}K_{(4)}X_3 - k_{-5}(K_{(3)})^2/(K_{(1)})^{0.5}) \\ &\times (K_{(7)}K_{(8)}K_{(11)})^{-1}X_1^{-0.5}X_2^2X_5)X_7^2, \end{aligned} \quad (5)$$

$$\begin{aligned} W_9 &= (k_{+9}(K_{(1)})^{0.5}(K_{(11)})^{-1}X_1^{0.5} \\ &- k_{-9}(K_{(10)})^{-1}X_4)X_7^2, \end{aligned} \quad (6)$$

where subscripts 1, 2, 3, 4, 5, and 6 correspond to the concentrations of non-Bodenstein substances (stable chemical compounds): oxygen, water, hydrogen, methane, carbon dioxide, and carbon oxide; subscripts 7, 8, 9, 10, 11, 12, 13, 14, and 15 correspond to Bodenstein substances (intermediate compounds that form on the surface of the catalyst).

The concentrations of intermediate compounds (7–15) are calculated through the concentrations of stable substances (1–6) by the following equations:

$$\begin{aligned} X_7 &= (1 + (K_{(1)})^{0.5}(X_1)^{0.5} + (K_{(3)})^{0.5}(X_2)^{0.5} \\ &+ (K_{(10)})^{-1}X_4 + K_{(4)}X_3 + (K_{(11)})^{-1}X_5 \\ &+ (K_{(1)})^{-0.5}(K_{(3)})^{1.5}(K_{(7)}K_{(8)}K_{(11)})^{-1}X_1^{-1}X_2^{1.5}X_5 \\ &+ K_{(3)}(K_{(7)}K_{(8)}K_{(11)})^{-1}X_2X_5 \\ &+ (K_{(3)})^{0.5}(K_{(8)}K_{(11)})^{-1}X_2^{0.5}), \end{aligned} \quad (7)$$

$$X_8 = (K_{(1)})^{0.5}(X_1)^{0.5}X_7, \quad (8)$$

$$X_9 = (K_{(3)})^{0.5}(X_2)^{0.5}X_7, \quad (9)$$

$$X_{10} = K_{(4)}X_3X_7, \quad (10)$$

$$\begin{aligned} X_{11} &= (K_{(1)})^{-0.5}(K_{(3)})^{1.5}(K_{(7)}K_{(8)}K_{(11)})^{-1} \\ &\times X_1^{-1}X_2^{1.5}X_5X_7, \end{aligned} \quad (11)$$

$$X_{12} = K_{(3)}(K_{(7)}K_{(8)}K_{(11)})^{-1}X_2X_5X_7, \quad (12)$$

$$X_{13} = (K_{(3)})^{0.5}(K_{(8)})^{-1}(K_{(11)})^{-1}X_2^{0.5}X_5X_7, \quad (13)$$

$$X_{14} = (K_{(11)})^{-1}X_5X_7, \quad (14)$$

$$X_{15} = (K_{(10)})^{-1}X_4X_7. \quad (15)$$

The equations of chemical invariants have the form

$$R_4^B = -2R_1^B + R_2^B + 3R_3^B, \quad (16)$$

$$R_5^B = 2R_1^B - R_2^B - 4R_3^B, \quad (17)$$

$$R_6^B = -R_2^B - 2R_3^B. \quad (18)$$

Consequently, the system of kinetic equations of the reaction of the steam–oxygen reforming of methane can be represented as a system of three first-order differential equations (1)–(3) and a system of three linear algebraic equations (16)–(18). This is completely determined if the initial conditions for all reactants are given. In this case, during the experiment, it is necessary to perform an analysis of the concentrations of only key substances.

Experimental study of the kinetics of the steam–oxygen reforming of methane. The kinetic experiment was carried out in MUCTR and Carberry gradientless catalytic reactors. GIAP-3 and GIAP-16 catalysts were studied in these reactors.

In conducting the experiments, the operating parameters were varied as follows: the volumetric flow rate of the feedstock from 300 to 1200 h⁻¹, pressure from 0.1 to 4.0 MPa, temperature from 750 to 1100°C, and the molar ratios of reactants H₂O/CH₄ from 0.8 to 1.2 and O₂/CH₄ from 0.55 to 1.0. The total number of the conducted experiments was 160. The analysis of the reaction products was performed by gas chromatography.

The estimation of the kinetic constants of the model was carried out using the least-squares method. The minimization of the function of many variables that characterizes the degree of the agreement of the results of the calculation and experiment was conducted using the Newton method and a random best-sample search. In particular, the constants for the reaction of the steam–oxygen reforming of methane at $T = 800^\circ\text{C}$ have the following values: $K_{(1)} = 0.13 \times 10^{-3} \text{ m}^3/\text{mol}$, $K_{(3)} = 0.02 \times 10^{-3} \text{ m}^3/\text{mol}$, $K_{(4)} = 0.30 \times 10^{-3} \text{ m}^3/\text{mol}$, $K_{(11)} = 1.78 \times 10^2 \text{ m}^3/\text{mol}$, $k_{+2} = 7.99 \times 10^2 \text{ s}^{-1}$, $k_{+5} = 2.07 \times 10^{-3} (\text{m}^3 \text{ s})/\text{mol}$, and $k_{+9} = 4.81 \times 10^{-2} (\text{m}^3 \text{ s})/\text{mol}$.

The verification of the adequacy of the model to the results of the experiment was performed using Bartlett's

test. It is shown that the model adequately reflects the kinetics of the reaction of the steam–oxygen reforming of methane in the entire range of the change of control variables.

Modeling of the steam–oxygen reforming of methane in a catalyst grain. For the mathematical description of the processes that occur in the grain of a catalyst in conducting the reaction of the steam–oxygen conversion of methane, a quasi-homogeneous model was chosen under the additional assumption that there is a cylindrical symmetry in the grain. In this case, for the granules of the catalyst such as Raschig rings, the model of the grain can be written as follows.

For the inner zone (zone I) of the catalyst, we have

$$\frac{d}{d\rho} \left(\rho D_{efi} \frac{dc_{li}}{d\rho} \right) = \rho R_i^B(\mathbf{c}_I, T_I), \quad i = 1, \dots, n, \quad (19)$$

$$\frac{d}{d\rho} \left(\rho \lambda_{ef} \frac{dT_I}{d\rho} \right) = \rho \sum_{u=1}^P \Delta H_u r_u(\mathbf{c}_I, T_I), \quad (20)$$

$$\rho = \tilde{r}, \quad c_{li}(\tilde{r}) = c_{gi}, \quad i = 1, \dots, n, \quad (21)$$

$$T_I(\tilde{r}) = T_g,$$

$$\rho = \tilde{r}_1, \quad \frac{dc_{li}}{d\rho} = 0, \quad i = 1, \dots, n, \quad (22)$$

$$\frac{dT_I}{d\rho} = 0.$$

For the outer zone (zone II) of the catalyst, we have

$$\frac{d}{d\rho} \left(\rho D_{efi} \frac{dc_{Iii}}{d\rho} \right) = \rho R_i^B(\mathbf{c}_{II}, T_{II}), \quad i = 1, \dots, n, \quad (23)$$

$$\frac{d}{d\rho} \left(\rho \lambda_{ef} \frac{dT_{II}}{d\rho} \right) = \rho \sum_{u=1}^P \Delta H_u r_u(\mathbf{c}_{II}, T_{II}), \quad (24)$$

$$\rho = \tilde{R}, \quad c_{Iii}(\tilde{R}) = c_{gi}, \quad i = 1, \dots, n, \quad (25)$$

$$T_{II}(\tilde{R}) = T_g,$$

$$\rho = \tilde{r}_1, \quad \frac{dc_{Iii}}{d\rho} = 0, \quad i = 1, \dots, n, \quad (26)$$

$$\frac{dT_{II}}{d\rho} = 0.$$

The additional conditions of the continuity of the solution are written as

$$\rho = \tilde{r}_1, \quad r < \tilde{r}_1 < \tilde{R}, \quad (27)$$

$$c_{li}(\tilde{r}_1) = c_{Iii}(\tilde{r}_1), \quad i = 1, \dots, n, \quad T_I(\tilde{r}_1) = T_{II}(\tilde{r}_1).$$

The set of equations (19)–(27) was transformed to the set of equations in the Cauchy normal form. A set of first-order equations was solved using the diagonal-implicit third-order methods. The construction of the solution of the transformed equations was carried out using the shooting

method with the minimization of the solution error in the inner and outer zones of the catalyst by the Newton method.

It is found that for a granule of industrial catalyst with the inner and outer diameters $d = 0.85$ cm and $D = 1.75$ cm, respectively, and the height $H = 1$ cm, the efficiency factors for methane are as follows: at $T = 800^\circ\text{C}$ $\eta = 0.21$; at $T = 900^\circ\text{C}$ $\eta = 0.16$; and at $T = 1000^\circ\text{C}$ $\eta = 0.14$. For the granules of the catalyst with the sizes $d = 0.5$ cm, $H = 1.2$ cm, and $D = 1$ cm, the values of the efficiency factors are as follows: at $T = 800^\circ\text{C}$ $\eta = 0.25$; at $T = 900^\circ\text{C}$ $\eta = 0.21$; and at $T = 1000^\circ\text{C}$ $\eta = 0.18$. Consequently, the efficiency factors monotonically increase with a decrease in the sizes of the granule.

As is known, in commercial plants with axial converters for maintaining the required profile of temperatures, it is necessary to ensure considerable linear flow velocities. As a consequence, to decrease the pressure drop over the bed, it is necessary to use granules of the catalyst with a sufficiently large diameter [3, 4]. For highly endothermic reactions, which mainly occur in the stern zones of such converters, the efficiency factors of the operation of the granules of the catalyst are negligible. This leads to a low production rate of the converters and a low degree of the use of raw materials as to carbon. Moreover, an examination of a number of operating plants that produce ammonia and methanol shows that the main reactions in the catalytic reaction zones occur on average in the first one-third of the reaction zone. The remaining portion of the loaded catalyst hardly participates in the reaction process. Therefore, the use of combined axial–radial reactors for the conversion of natural gas to synthesis gas appears to be promising.

Mathematical model of an autothermal reactor. The model can be written as

$$\frac{dn_{gi}}{dl} = S_r k_{gi} S_{gs} (y_{gi} - y_{si}), \quad i = 1, \dots, n, \quad (28)$$

$$k_{gi} S_{gs} (y_{gi} - y_{si}) = \rho_B \eta_i R_i^B(\mathbf{y}_s, T_s), \quad i = 1, \dots, n, \quad (29)$$

$$u_g C_{pg} \rho_g \frac{dT_g}{dl} + \alpha S_{gs} (T_g - T_s) = 0, \quad (30)$$

$$\lambda_{aef} \frac{d^2 T_s}{dl^2} - \alpha S_{gs} (T_g - T_s) + \sum_{u=1}^P \eta_u \Delta H_u r_u(\mathbf{y}_s, T_s) = 0. \quad (31)$$

The initial conditions are as follows:

$$l = 0, \quad n_{gi}(0) = n_{gi0}, \quad i = 1, \dots, n, \quad T_g(0) = T_{g0}. \quad (32)$$

The boundary conditions are written as

$$l = 0, \quad T_s(0) = T_{s0}, \quad (33)$$

$$l = L, \quad \frac{dT_s}{dl} = 0. \quad (34)$$

Replacing the axial coordinate l by the radial coordinate r in the set of equations (28)–(34), we obtain the mathematical model of the radial section of the reactor. The model has the form

$$-\frac{1}{r} \frac{d(u_g c_{gi} r)}{dr} = k_{gi} S_{gs} (y_{gi} - y_{si}), \quad i = 1, \dots, n, \quad (35)$$

$$k_{gi} S_{gs} (y_{gi} - y_{si}) = \rho_B \eta_i R_i^B(\mathbf{y}_s, T_s), \quad i = 1, \dots, n, \quad (36)$$

$$\frac{1}{r} \frac{d(u_g C_{pg} \rho_g r T_g)}{dr} = \alpha S_{gs} (T_g - T_s), \quad (37)$$

$$\begin{aligned} \frac{1}{r} \frac{d}{dr} \left(\lambda_{ref} r \frac{dT_s}{dr} \right) - \alpha S_{gs} (T_g - T_s) \\ + \sum_{u=1}^P \eta_u \Delta H_u r_u(\mathbf{y}_s, T_s) = 0. \end{aligned} \quad (38)$$

The initial conditions are as follows:

$$\begin{aligned} r = r_0, \quad c_{gi}(r_0) = c_{gi0}, \quad i = 1, \dots, n, \\ T_g(r_0) = T_{g0}. \end{aligned} \quad (39)$$

The boundary conditions are written as

$$r = r_0, \quad T_s(r_0) = T_{s0}, \quad (40)$$

$$r = R, \quad \frac{dT_s}{dl} = 0. \quad (41)$$

To determine the macrokinetic parameters of the above models, extensive bench and trial experiments were performed at the following enterprises: AO Permnefteorgsintez, AO Salavatnefteorgsintez, AO Nizhnekamskneftekhim, and AO Azot. It is shown that with the use of certain macrokinetic parameters, the constructed models reflect the available experimental data with an accuracy that is sufficient for practice.

The modes of the operation of the autothermal reactor that ensure a content of carbon oxide in the product synthesis gas of more than 20 vol % at a hydrogen concentration of more than 42 vol % were analyzed using the constructed models. In this case, the specific yield of synthesis gas was more than 3.0. Oxygen-saving modes of the operation of the reactor at a molar ratio of oxygen to methane in the original gas of less than 0.65 were also analyzed. It is shown that the dilution of the feedstock with nitrogen makes it possible to organize the process of the production

of synthesis gas with smaller values of temperature warming than those using pure oxygen.

An analysis of the operation of the autothermal reactors made it possible to design a catalytic reactor that allows the volume of the catalyst to be reduced for the given production rate of the reactor by 20% in comparison with conventional industrial apparatuses (the geometrical dimensions of a new reactor decrease accordingly); to obtain a molar H_2/CO ratio of more than 2.06 and a molar CO/CO_2 ratio of more than 3 in the product synthesis gas, and from synthesis gas with such a content of reactants it is possible to produce high-quality methanol with the concentration of methanol in raw methanol of more than 95 wt %; to reduce specific expenditures on methane in the production of synthesis gas by 15% in comparison with the known commercial processes, with the prime cost of produced methanol being decreased by 10–15%; to lower the material consumption of new autothermal catalytic reactors by 10–15%; and to develop the designs of catalytic reactors taking into account the possibilities of their manufacture at the machine-building factories of the Russian Federation.

MODELING OF METHANOL PRODUCTION FROM SYNTHESIS GAS

At present, the main quantity of methanol in the world is produced according to the technologies of various companies using low-temperature copper-zinc catalysts [5–7]. A catalytic process of the production of methanol is implemented in a partitioned flow reactor. The conversion of synthesis gas in such a reactor is not high: from 3 to 15%. The temperature differences in the sections reach 50–70°C. In view of the low conversion of synthesis gas, it is necessary to recycle the unreacted feedstock. The volumetric flow rate of the recycled stream is higher than the volumetric flow rate of the feedstock by a factor of 8–15. The quality of the produced raw methanol is low, which impedes its purification.

Therefore, the main purpose of the modeling of methanol production was associated with the organization of a one-pass process of the synthesis of high-quality methanol without feedstock recirculation at a synthesis gas conversion of higher than 75–80%. A further considerable decrease in the prime cost of the target product of methanol is possible only at such characteristics of the operation of the reactor unit.

The modeling of methanol production from synthesis gas according to the principles of systems analysis is performed by the following stages: 1) analysis of the kinetic regularities of the occurrence of the reaction of methanol synthesis and the construction of the kinetic model of the reaction, 2) analysis of the reaction of methanol synthesis in the grain of a copper-containing catalyst and the construction of the model of the grain, and 3) analysis of the process in a catalytic shell-and-tube reactor and the construction of the model of the reactor.

Kinetic model of methanol synthesis. The kinetic model of the reaction of methanol synthesis is constructed accord-

ing to the seven-stage mechanism of this reaction, which includes five stable substances (hydrogen, carbon dioxide, carbon oxide, water, and methanol) and six intermediate complexes with numbers 6–11. Since the rank of the matrix of the overall equations is two, there are only two key substances, as which hydrogen and carbon oxide were chosen. The rates of the variation of their concentrations are expressed as the linear combinations of the rates of slow elementary reactions:

$$R_1^B = -W_3 - 3W_7 = -k_{+3}X_8 + k_{-3}X_9X_3 - 3[k_{+7}X_{11}X_4 - k_{-7}X_5X_9], \quad (42)$$

$$R_3^B = W_3 = k_{+3}X_8 - k_{-3}X_9X_3. \quad (43)$$

For intermediate compounds and auxiliary variables, we have

$$n_1 = \frac{k_{+7}K_{(6)}X_1X_4}{k_{+3} + k_{-2}}, \quad (44)$$

$$n_2 = \frac{k_{-7}}{K_4k_{+5}} \frac{X_4X_5}{X_1}, \quad (45)$$

$$n_3 = \frac{(k_{-3}X_3 + k_{-7}X_5)(K_4)^{-1}X_4 + k_{+2}X_2K_1X_1}{k_{+3} + k_{-2}}, \quad (46)$$

$$n_4 = \frac{k_{-5}X_4}{k_{+5}X_1} + \frac{K_6k_{+7}X_4}{k_{+5}}, \quad (47)$$

$$X_6 = \frac{1.0}{\left(1.0 + K_{(6)}X_1 + \frac{n_4(n_2 + n_3)}{n_1 + n_4} - n_2 + \frac{X_4}{K_{(4)}} + \frac{(n_2 + n_3)(K_{(6)} + 1.0)}{n_1 + n_4}\right)}, \quad (48)$$

$$X_7 = K_{(6)}X_1X_6, \quad (49)$$

$$X_8 = \left(\frac{n_4(n_2 + n_3)}{n_1 + n_4} - n_2\right)X_6, \quad (50)$$

$$X_9 = \frac{X_4X_6}{K_{(4)}}, \quad (51)$$

$$X_{10} = \left(\frac{n_2 + n_3}{n_1 + n_4}\right)X_6, \quad (52)$$

$$X_{11} = K_{(6)}X_1X_{10}. \quad (53)$$

The rates of the variation of the concentrations of non-key substances are determined through the rates of the variation of the concentrations of key substances according to the following equations of chemical invariants:

$$R_2^B = \frac{1}{3}R_1^B - \frac{2}{3}R_3^B, \quad (54)$$

$$R_4^B = -\frac{1}{3}R_1^B + \frac{2}{3}R_3^B, \quad (55)$$

$$R_5^B = -\frac{1}{3}R_1^B - \frac{1}{3}R_3^B. \quad (56)$$

The kinetics of methanol synthesis on promoted copper-zinc catalysts was studied in flow and flow-circulation reactors in the ranges of the variation of pressure from 0.6 to 6.0 MPa, temperature from 373 to 653 K, volumetric flow rate from 500 to 2000 h⁻¹, and molar hydrogen/carbon

oxide ratio from 5.0 to 1.5. The total number of experiments was 50. The analysis of the reaction products was performed by gas chromatography.

The constants of the kinetic model were estimated from the results of experiments by the nonlinear least-squares method. The minimization of the function of many variables that characterizes the degree of the agreement of the results of the calculation and experiment was conducted using the random best-sample search and the simplex method.

In particular, for the conditions of conducting the experiment at $P = 6.0$ MPa and $T = 503$ K, the constants have the following values:

for methanol synthesis, $K_{p\text{ met}} = 1.4 \times 10^{-2}$ atm⁻²;

for the steam conversion of carbon oxide, $K_{p\text{ shift}} = 1.28 \times 10^2$;

for the elementary stages, $k_{(+2)} = 7.73 \times 10^2$ s⁻¹, $k_{(-2)} = 1.18 \times 10^2$ atm/s, $k_{(+3)} = 1.16 \times 10^1$ atm/s, $k_{(+5)} = 3.54 \times 10^2$ s⁻¹, and $k_{(+7)} = 3.64 \times 10^3$ s⁻¹.

The model verification using Bartlett's test has shown that the model is in complete agreement with the experiment in the chosen region of experimentation.

Modeling of methanol synthesis in the grain of a catalyst. A quasi-homogeneous model was used as the model of the grain. It was assumed that the grain of the catalyst has a cylindrical symmetry. For the equations of the model of the grain, the equations of diffusion stoichiometry that make it possible to reduce the dimensionality of the set of equations from 6 to 2 were additionally determined. The equations of the model of the grain were integrated using the implicit third-order Runge–Kutta method. The profiles of the concentrations of reactants and temperature in the

granule were determined by the shooting method. It has been shown that the efficiency factors of the operation of the grain in the chosen region of experimentation are in the range of 0.65–0.9 for granule diameters of 5×10^{-3} m and exceed 1 for granule diameters of more than 1×10^{-2} m.

Modeling of the of methanol production reactor unit. The preliminary experiments performed using bench reactors have shown that in shell-and-tube apparatuses in carrying out the process of methanol synthesis at small axial temperature gradients, it is possible to produce raw methanol with a high methanol content and with trace quantities of organic impurities. Such raw methanol can, first, already be the target product and, second, can be purified to a product with a methanol content of 99.9 wt % or higher without large energy expenditures.

Shell-and-tube reactors are inexpensive and simple for operation and repair and allow for high-efficiency catalysts to be used. The catalysts used in the reactors of such designs have the longest duration of operation.

A three-reactor unit of the conversion of synthesis gas that consists of three shell-and-tube reactors has been developed. In this unit, water is used as a heat transfer medium. Each shell-and-tube reactor is provided with two elements: a heat exchanger and a condenser-cooler. Before the supply to the reactor, the feedstock passes through a heat exchanger in which it is heated up to the reaction temperature by the hot product flow that leaves the reactor. The product flow is then supplied to the condenser-cooler in which methanol condenses, and noncondensable synthesis gas is supplied to the subsequent reactor. Due to the high exothermicity of the reaction of the conversion of synthesis gas, water in the intertubular space of the shell-and-tube reactor boils with the formation of steam with a pressure of 2.0 MPa. In producing 1 t of methanol, 0.7 t of steam forms. This can be used in steam turbines or as a heat transfer medium in various sections of a unit for producing engine fuels. Methanol from condensers-coolers is collected in a single vessel, and from this it is either is transferred to a user or is supplied to further processing. The total conversion of synthesis gas in three reactors is not less than 75–80%. The remaining synthesis gas is supplied to a gas turbine for power production.

It should be emphasized that the raw methanol produced according to the new technology has a high purity; as a consequence, for a number of productions, it can be either a marketable product, for example, for the gas industry, or feedstock for producing dimethyl ether, ethylene, propylene, and engine fuels. For the produced high-purity methanol, the number and volume of industrial distillation columns decrease considerably, which leads to a reduction in the metal consumption and a decrease in power inputs.

Moreover, since the process of the production of methanol occurs according to the scheme without feedstock recirculation, there is no necessity for using power-consuming recycling. This also favors an increase in the profitability of methanol production. Finally, since the production of methanol on the whole is carried out under mild conditions of methanol synthesis, the duration of the operation of industrial catalysts also increases.

MODELING OF DIMETHYL ETHER PRODUCTION FROM METHANOL

Dimethyl ether is a colorless nontoxic gas that rapidly decomposes in the atmosphere. It has a low autoignition temperature and a high cetane number [8]. When it is used as diesel fuel, the cardinal redesign of an engine is not required and the quantity of harmful emissions into the environment during the operation of the engine decreases sharply. The amount of harmful emissions is also substantially lowered when DME is used as a household gas. In recent years, the demand for DME steadily increases.

There are several methods for DME production: directly from synthesis gas and from methanol. DME production by the dehydration of methanol is implemented in industry. It is carried out at increased pressures and temperatures of 2260–300°C. In this temperature range, it is not possible to reach a high selectivity of the process and a considerable degree of the conversion of the feedstock, since the equilibrium concentration of methanol in the product flow increases with a rise in temperature. In particular, because of this, the prime cost of produced DME is rather high. It can be substantially reduced if the dehydration of methanol is carried out at 110–170°C. In this case, a high purity of produced DME at a high degree of methanol conversion and a sharp decrease in power inputs is attained. A new catalyst for the dehydration of methanol is developed that ensures a methanol conversion close to the equilibrium value at low temperatures and a GHSV of 300–1500 h⁻¹. In this case, the stage of DME purification is abruptly simplified, and, if there is a need for producing high-purity DME, the stage of water purification from methanol is also simplified when its use in production as service water is necessary. The organization of methanol dehydration according to this scheme leads to a considerable (15–20%) decrease in the prime cost of DME and makes this chemical product competitive in the world market.

Kinetic model of DME synthesis. A four-stage scheme of the reaction of methanol dehydration is proposed, in accordance with which a kinetic model of the reaction is constructed. The kinetic model is written as

$$R_{\text{CH}_3\text{OH}}^B = \frac{-2k_{+2}(K_{(1)})^2 c_{\text{CH}_3\text{OH}}^2 + 2k_{-2}(K_{(3)})^{-1}(K_{(4)})^{-1} c_{\text{CH}_3\text{OCH}_3} c_{\text{H}_2\text{O}}}{(1 + K_{(1)} c_{\text{CH}_3\text{OH}} + (K_{(3)}) c_{\text{CH}_3\text{OCH}_3} + (K_{(4)}) c_{\text{H}_2\text{O}})^2}. \quad (57)$$

Methanol is chosen as the key substance, and dimethyl ether and water can be determined from the equations of chemical invariants:

$$R_{\text{H}_2\text{O}}^B = -\frac{R_{\text{CH}_3\text{OH}}^B}{2}, \quad (58)$$

$$R_{\text{CH}_3\text{OCH}_3}^B = -\frac{R_{\text{CH}_3\text{OH}}^B}{2}. \quad (59)$$

The experimental study of the kinetics of the reaction of methanol dehydration was carried out in a laboratory isothermal reactor with a diameter of 10 mm and a length of 200 mm. The volume of the catalyst was 10–12 cm³. The operating parameters were varied as follows: the volumetric rate of the supply of the liquid phase from 0.5 to 12.5 h⁻¹, the temperature of the flow from 90 to 200°C, and the pressure in the reactor from 0.1 to 1.0 MPa. Both pure methanol and water–methanol mixtures in which the water content did not exceed 20 wt % were used as the feedstock. The analysis of the feedstock and the reaction products was performed by gas chromatography. The total number of conducted experiments was 20. A separate series of experiments were aimed at studying the duration of the operation of the catalyst. It is shown that the activity of the catalyst remains almost constant within 4000 h. On the basis of the results of experiments, the parameters of the kinetic model were estimated using the nonlinear least-squares method.

In this case, the equilibrium constants were expressed as

$$\begin{aligned} K_p &= e^{-\Delta S/R} e^{\Delta H/RT}, \quad K_{(1)} = e^{-ko(1) + ko(1)/RT}, \\ K_{(3)} &= e^{-ko(3) + ko(4)/RT}, \quad K_{(4)} = e^{-ko(5) + ko(6)/RT}, \\ K_{\text{complex1}} &= k_{+2}(K_{(1)})^2 = e^{ko(7) - ko(8)/RT}, \\ K_{\text{complex2}} &= (K_{(3)})^{-1}(K_{(4)})^{-1} = e^{-ko(9) - ko(10)/RT}. \end{aligned}$$

As a result of the calculation using a program, the numerical values of the kinetic constants were found: $ko(1) = 13.84$, $ko(2) = 9221.37$, $ko(3) = 7.62$, $ko(4) = 503.99$; $ko(5) = 20.58$; $ko(6) = 16915.73$; $ko(7) = 17.73$; $ko(8) = 12887.14$; $ko(9) = 18.59 \times 10^{-5}$, and $ko(10) = 2878.79$.

Model of a catalytic reactor for DME synthesis. Upon the completion of the investigational phase concerned with studying the process of the chemical conversion itself, we pass to its analysis in the grain of the catalyst and in a catalytic reactor. A quasi-homogeneous model was used as the model of the grain. The macrokinetic parameters of the model were calculated by the known correlation equations, and their values were refined further on the basis of experimental data. Using this model, the values of the efficiency factors of methanol for the granules of the catalyst with cylindrical symmetry were calculated. It turned out that the values of the efficiency factors were approximately 0.76 for the temperature range 110–130°C and 0.84 for the temperature range 150–170°C.

The rate of the variation of the concentrations of methanol, DME, and water can be expressed as

$$R_{\text{CH}_3\text{OH}}^B = -2r_1, \quad (60)$$

$$R_{\text{CH}_3\text{OCH}_3}^B = r_1, \quad (61)$$

$$R_{\text{H}_2\text{O}}^B = r_1. \quad (62)$$

Then, the model of the catalytic reactor of the process of methanol dehydration is as follows:

for the gas phase

$$D_a \frac{d^2 c_{gi}}{dl^2} - u_g \frac{dc_{gi}}{dl} + k_{gi} S_{gs} (c_{gi} - c_{si}) = 0, \quad (63)$$

$$i = 1, \dots, n,$$

$$\lambda_a \frac{dT_g}{dl^2} - u_g C_{pg} \rho_g \frac{dT_g}{dl} + \alpha S_{gs} (T_g - T_s) = 0. \quad (64)$$

and for the solid phase

$$k_{si} S_{gs} (c_{gi} - c_{si}) = \eta_i R_i^B(\mathbf{c}_s, T_s), \quad i = 1, \dots, n, \quad (65)$$

$$\alpha S_{gs} (T_g - T_s) = \sum_{u=1}^P \eta_u \Delta H_u r_u(\mathbf{c}_s, T_s). \quad (66)$$

The boundary conditions are written as

$$l = 0, \quad u_g (c_{gi0} - c_{gi}) = -D_a \frac{dc_{gi}}{dl}, \quad (67)$$

$$i = 1, \dots, n,$$

$$u_g C_{pg} \rho_g (T_{g0} - T_g) = -\lambda_a \frac{dT_g}{dl}, \quad (68)$$

$$l = L, \quad \frac{dc_{gi}}{dl} = 0, \quad i = 1, \dots, n, \quad \frac{dT_g}{dl} = 0. \quad (69)$$

The numerical values of the macrokinetic parameters of the model were calculated beforehand using correlation equations and were then refined on the basis of the results of additionally performed experiments. The conducted calculations of the operating modes of the industrial reactor of DME production from methanol and the methanol–water, methanol–DME, and methanol–DME–water mixtures have shown that there are operating modes of the catalytic reactor that ensure the almost complete purification of water from methanol. In this case, concentrated DME with a water impurity and a small methanol content is produced.

MODELING OF THE PRODUCTION OF ENGINE FUELS FROM DIMETHYL ETHER AND METHANOL

In world practice, all processes of the chemical conversion of natural gas to liquid compounds are placed into one category of chemical processes (Gas to Liquids—GTL) [9].

The prospects of the development and introduction of GTL processes in the world and in Russia are stipulated by the following causes: 1) a decrease in oil extraction that is

predicted for the period between 2010 and 2020 with a simultaneous increase in the demand for engine fuels, 2) a toughening of the ecological requirements regarding the quality of engine fuels, and 3) the necessity for developing distant hard-to-reach and low-pressure natural gas fields.

As is known, high-octane engine fuels produced from petroleum are obtained as a result of the compounding of individual fractions in certain ratios. The first fraction is called reformat gasoline and mainly consists of aromatic high-octane hydrocarbons. The second fraction is called isomerization gasoline and mainly consists of *iso*- and *n*-alkane hydrocarbons of the pentane–hexane fraction of petroleum. The third fraction is called alkylation gasoline and mainly consists of isoalkane hydrocarbons of the C_7 – C_9 fraction.

Isomerization gasoline and alkylation gasoline are indispensable components of automotive gasoline, since, when they are used, the quantity of harmful emissions (carbon oxides, nitrogen, and finely divided carbon) into the environment abruptly decreases.

It should also be emphasized that the content of sulfur and nitrogen-containing organic compounds in the components of car fuels produced from natural gas does not exceed 0.001 wt %. Therefore, the use of such fuels leads to a sharp decrease of atmospheric pollution, which is very important for the large megacities of the world.

Note that the complex processing of gas condensate deposits, especially in the Polar region of Western Siberia, is promising. Many of them have gas condensates with a high content of light hydrocarbons. Therefore, the compounding of the high-octane hydrocarbon fractions obtained in processing natural gas with the pentane–hexane fraction of gas condensate subjected beforehand to the process of isomerization and the fraction of C_7 – C_9 hydrocarbons (with an octane number of 55–65) makes it possible to produce gasolines of Euro-4 grade at considerably lower prices in comparison with the world prices.

Kinetic model of the synthesis of engine fuels. In accordance with the principles of the systems analysis of catalytic processes, the general kinetic model of the synthesis of engine fuels from methanol is divided into the following submodels: 1) DME synthesis from methanol at an elevated temperature [10], 2) olefin synthesis from DME and methanol [10], 3) the synthesis of isoalkane hydrocarbons from olefins [11], and 4) the synthesis of aromatic hydrocarbons from olefins [11].

The stage mechanism of the reaction of the synthesis of DME and lower olefins from methanol, the respective kinetic model, and the constants of the model are presented in [10], and the kinetic model of the synthesis of isoalkane hydrocarbons from olefins is given in [11].

The kinetic model of the reaction of the production of aromatic and naphthenic hydrocarbons from lower olefins is constructed according to the stage mechanism of the reaction of their conversion that includes 45 elementary stages reflecting the reactions of oligomerization, disproportionation, ring formation, dehydrogenation, dehydrocy-

clization, hydrogenation, and the cracking of hydrocarbons. The following substances were chosen as the non-Bodenstein substances of these reactions:

ethylene	$CH_2=CH_2$	X_1 ,
propylene	$CH_3-CH=CH_2$	X_2 ,
butene-1	$CH_3-CH_2-CH=CH_2$	X_3 ,
pentene-1	$CH_3-CH_2-CH_2-CH=CH_2$	X_4 ,
cyclohexane	C_6H_{12}	X_5 ,
methylcyclohexane	$(CH_3)C_6H_{11}$	X_6 ,
dimethylcyclohexane	$(CH_3)_2C_6H_{10}$	X_7 ,
trimethylcyclohexane	$(CH_3)_3C_6H_9$	X_8 ,
tetramethylcyclohexane	$(CH_3)_4C_6H_8$	X_9 ,
benzene	C_6H_6	X_{10} ,
toluene	$(CH_3)C_6H_5$	X_{11} ,
xylene	$(CH_3)_2C_6H_4$	X_{12} ,
mesitylene	$(CH_3)_3C_6H_3$	X_{13} ,
durene	$(CH_3)_4C_6H_2$	X_{14} ,
hydrogen	H_2	X_{15} .

The rates of the variation of the concentrations of these substances have the form

$$R_1^B = -r_1 - r_6, \quad (70)$$

$$R_2^B = -r_1 - 2r_2 - r_3 - 3r_5 - r_6, \quad (71)$$

$$R_3^B = -r_3 - 2r_4, \quad (72)$$

$$R_4^B = r_1 - r_6, \quad (73)$$

$$R_5^B = r_2 - r_7, \quad (74)$$

$$R_6^B = r_3 - r_8, \quad (75)$$

$$R_7^B = r_4 - r_9, \quad (76)$$

$$R_8^B = r_5 - r_{10}, \quad (77)$$

$$R_9^B = r_6 - r_{11}, \quad (78)$$

$$R_{10}^B = r_7, \quad (79)$$

$$R_{11}^B = r_8, \quad (80)$$

$$R_{12}^B = r_9, \quad (81)$$

$$R_{13}^B = r_{10}, \quad (82)$$

$$R_{14}^B = r_{11}, \quad (83)$$

$$R_{15}^B = 3(r_7 + r_8 + r_9 + r_{10} + r_{11}). \quad (84)$$

The equations of chemical invariants are written as

$$R_1^B = -R_4^B - 2R_9^B - 2R_{14}^B, \quad (85)$$

$$R_2^B = -R_4^B - 2R_5^B - R_6^B - 3R_8^B - 2R_9^B - 2R_{10}^B - 3R_{13}^B - 2R_{14}^B, \quad (86)$$

$$R_3^B = -R_6^B - 2R_7^B - R_{11}^B - 2R_{12}^B, \quad (87)$$

$$R_{15}^B = 3R_{10}^B + 3R_{11}^B + 3R_{12}^B + 3R_{13}^B + 3R_{14}^B. \quad (88)$$

The rates of the route reactions are expressed as

$$r_1 = (k_{+5}K_{(1)}K_{(4)}X_1X_2 - k_{-5}X_4)X_{16}, \quad (89)$$

$$r_2 = (k_{+11}K_{(2)}K_{(6)}X_2^2 - k_{-11}X_5)X_{16}, \quad (90)$$

$$r_3 = (k_{+12}K_{(3)}K_{(7)}X_2X_3 - k_{-12}X_6)X_{16}, \quad (91)$$

$$r_4 = (k_{+13}K_{(3)}K_{(8)}X_3^2 - k_{-13}X_7)X_{16}, \quad (92)$$

$$r_5 = (k_{+14}K_{(2)}K_{(6)}K_{(9)}X_2^3 - k_{-14}X_8)X_{16}, \quad (93)$$

$$r_6 = (k_{+15}K_{(1)}K_{(4)}K_{(10)}X_1X_2X_4 - k_{-15}X_9)X_{16}, \quad (94)$$

$$r_7 = (k_{+16}X_5 - k_{-15} \times (K_{(17)}K_{(18)}K_{(19)}K_{(20)}K_{(21)})^{-1}X_{10}X_{15}^3)X_{16}, \quad (95)$$

$$r_8 = (k_{+22}X_6 - k_{-22} \times (K_{(23)}K_{(24)}K_{(25)}K_{(26)}K_{(27)})^{-1}X_{11}X_{15}^3)X_{16}, \quad (96)$$

$$r_9 = (k_{+28}X_7 - k_{-28} \times (K_{(29)}K_{(30)}K_{(31)}K_{(32)}K_{(33)})^{-1}X_{12}X_{15}^3)X_{16}, \quad (97)$$

$$r_{10} = (k_{+34}X_8 - k_{-34} \times (K_{(35)}K_{(36)}K_{(37)}K_{(38)}K_{(39)})^{-1}X_{13}X_{15}^3)X_{16}, \quad (98)$$

$$r_{11} = (k_{+40}X_9 - k_{-40} \times (K_{(40)}K_{(41)}K_{(42)}K_{(43)}K_{(44)})^{-1}X_{14}X_{15}^3)X_{16}, \quad (99)$$

where X_{16} is the active site of the catalyst.

Laboratory kinetic experiments were carried out in a Carberry-type flow-circulation reactor; an MUCTR flow-circulation reactor, which makes it possible to perform experiments at a pressure of up to 60 atm and temperatures up to 650°C; and an integral flow reactor. In conducting the experiments, the volumetric rate of the supply of the feedstock for the liquid was varied from 0.5 to 3 h⁻¹, the pressure in a reactor was varied from 0.1 to 3.0 MPa, and the temperature of the reaction medium was varied from 280 to 480°C. The composition of the feedstock and the catalyst was analyzed by gas chromatography. The total number of performed kinetic experiments was 22.

By a series of experiments conducted earlier, it is found that for high-silicon zeolites at temperatures of 360–500°C, the degree of the conversion of methanol and DME is not less than 95%. In this case, more than 70% of the feedstock is converted to olefinic hydrocarbons (ethene, propene, and butene).

In studying the reaction of the conversion of olefins to the hydrocarbons of engine fuels, the clusters of nickel and/or iron and carbon were applied to the surface of the crystals of zeolites. It is shown that the clusters stabilize the operation of the catalyst and the duration of its service increases up to 1000–1500 h. Under the conditions specified above, the degree of the conversion of olefins is not less than 98% at the end of the operation cycle and 99.9% with the use of the fresh catalyst. The conversion of pure DME is not less than 95% (99.6% at the beginning of the operation cycle).

The constants of the kinetic model were calculated using experimental data as the complexes of constants $ko(1)$ – $ko(22)$ by the least-squares method. The differential equations of the model were solved using the semi-implicit fourth-order Runge–Kutta method. The minimization of the functional that characterizes the adequacy of the model to experiment was performed using the Newton method and the random best-sample search. It is shown that the model prediction is in good agreement with the experiment.

The numerical values of the complexes of constants at $T = 450^\circ\text{C}$ are as follows (the concentrations of non-Bodenstein substances are expressed in atm):

$$ko(1) = k_{+5}K_{(1)}K^{(4)} = 29.22; ko(2) = k_{-5} = 0.280;$$

$$ko(3) = k_{+11}K_{(2)}K_{(6)} = 10.874; ko(4) = k_{-11} = 13.21;$$

$$ko(5) = k_{+12}K_{(3)}K_{(7)} = 8.61; ko(6) = k_{-12} = 0.01;$$

$$ko(7) = k_{+13}K_{(3)}K_{(8)} = 60.1; ko(8) = k_{-13} = 0.01;$$

$$ko(9) = k_{+14}K_{(2)}K_{(6)}K_{(9)} = 28.4; ko(10) = k_{-14} = 0.9198;$$

$$ko(11) = k_{+15}K_{(1)}K_{(4)}K_{(10)} = 10.0; ko(12) = k_{-15} = 1.257;$$

$$ko(13) = k_{+16} = 9.284;$$

$$ko(14) = k_{-16}(K_{(17)}K_{(18)}K_{(19)}K_{(20)}K_{(21)})^{-1} = 3.815;$$

$$ko(15) = k_{+22} = 0.6869;$$

$$ko(16) = k_{-22}(K_{(23)}K_{(24)}K_{(25)}K_{(26)}K_{(27)})^{-1} = 0.01;$$

$$ko(17) = k_{+28} = 4.127;$$

$$ko(18) = k_{-28}(K_{(29)}K_{(30)}K_{(31)}K_{(32)}K_{(33)})^{-1} = 0.006;$$

$$ko(19) = k_{+34} = 12.84;$$

$$ko(20) = k_{-34}(K_{(35)}K_{(36)}K_{(37)}K_{(38)}K_{(39)})^{-1} = 7.613;$$

$$ko(21) = k_{+40} = 5.277;$$

$$ko(22) = k_{-40}(K_{(41)}K_{(42)}K_{(43)}K_{(44)}K_{(45)})^{-1} = 4.759.$$

Modeling of the production of engine fuels in the grain of a catalyst. The used catalyst (a new high-silicon zeolite KRM-3 catalyst) is characterized by a fine-crystalline narrow-pore structure. The catalyst makes it possible to convert a wide range of raw materials into hydrocarbons. In this way, high-octane fractions of hydrocarbons (the octane number is 90–91) are produced from gas condensate, and the propane–butane fraction is converted to alkylaromatic hydrocarbons.

To calculate the efficiency factors, the quasi-homogeneous model of the grain was used.

The values of the efficiency factors for individual reactants (at $T = 450^\circ\text{C}$ and $P = 3.0$ MPa) were as follows: 1.02 for methanol, 1.01 for dimethyl ether, 0.99 for ethylene, 0.98 for propylene, 0.97 for butylene, 0.95 for cyclohexane, 0.92 for methyl cyclohexane, 0.92 for benzene, 0.89 for toluene and xylenes, 0.87 for trimethylbenzenes, and 0.86 for tetramethylbenzenes.

Design of a catalytic reactor for the synthesis of engine fuels and the modes of its operation. The temperature gradients along the radius and axis of the reactor play an important role in this process. If they exceed a certain value, the quality of produced engine fuel and the duration of the catalyst operation without regeneration abruptly decrease. The technology requires the elimination of the formation of the zones of local excessive heating in the bed. Such zones are called hot spots. It is experimentally shown that the quality of the products of the conversion of dimethyl ether and methanol to gasoline hydrocarbons in a fixed bed of the catalyst is usually higher in the cases where the profile of the temperature in the reaction zone uniformly increases along the axis of the reactor from its inlet to the outlet. This requirement should be met for all values of the radii of a cylindrical reactor.

It is proposed to use polytropic shell-and-tube reactors in the developed technology for the process of the synthesis of fuels. They are simple in manufacture, and for heat removal they use a heat transfer medium that circulates in the intertubular space of the reactor. Organic high-boiling compounds, water, and melts of salts can be chosen as a heat transfer medium. Due to the selection of a heat transfer medium, a particular thermal regime of the operation of the reactor is ensured.

Model of a catalytic reactor for the synthesis of engine fuels. The model of the reactor is written as

$$u_g \frac{\partial \mathbf{c}_g}{\partial l} + D_r \left(\frac{\partial^2 \mathbf{c}_g}{\partial r^2} + \frac{1}{r} \frac{\partial \mathbf{c}_g}{\partial r} \right) - [k_g] S_{gs} (\mathbf{c}_g - \mathbf{c}_s) = 0, \quad (100)$$

$$u_g C_{pg} \rho_g \frac{\partial T_g}{\partial l} + \lambda_r \left(\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r} \frac{\partial T_g}{\partial r} \right) - \alpha S_{gs} (T_g - T_s) = 0, \quad (101)$$

$$[\eta] \mathbf{R}^B(\mathbf{c}_s, T_s) = [k_g] S_{gs} (\mathbf{c}_g - \mathbf{c}_s), \quad (102)$$

$$\sum_{u=1}^P \eta_u \Delta H_u r_u(\mathbf{c}_s, T_s) = \alpha S_{gs} (T_g - T_s). \quad (103)$$

The boundary conditions are as follows:

$$l = 0, \quad \mathbf{c}_g(0, r) = \mathbf{c}_{g0}(r), \quad T_g(0, r) = T_{g0}(r), \quad (104)$$

$$r = 0, \quad \frac{\partial \mathbf{c}_g}{\partial r} = 0, \quad \frac{\partial T_g}{\partial r} = 0, \quad (105)$$

$$r = R, \quad \frac{\partial \mathbf{c}_g}{\partial r} = 0, \quad \lambda_r \frac{\partial T_g}{\partial r} \bigg|_R = \alpha (T_g - T_s). \quad (106)$$

On the basis of the results of modeling, a system of measures for controlling the catalytic process is developed that ensures the operational stability of the reactor and the production of high-octane gasoline of the required quality, namely, the formation of hot zones should be only in the final beds in the reactor; the temperature between the heat transfer medium and the reaction flow should be higher than 20°C ; and the temperature difference along the radius of the reaction tube should not exceed $5\text{--}7^\circ\text{C}$.

Using the model, the main dimensions of the catalytic reactor for the synthesis of engine fuels are calculated. The reactor is made of nickel-chrome steel, the diameter of the tubes is 32–40 mm, and the height of the tubes is 4–10 m. The tubes of the reactor are filled with a new zeolite catalyst. It is proposed to provide the reactor unit with two additional catalytic reactors in which the production of mainly isoalkane $\text{C}_4\text{--C}_9$ hydrocarbons, which correspond to alkylation gasoline, is carried out. On the basis of the conducted laboratory studies, isoalkane hydrocarbons that are close in composition to the hydrocarbons of alkylation gasoline were mainly produced at a temperature of 350°C for zeolite catalysts with the sizes of zeolite crystals of about $1 \mu\text{m}$ that are additionally promoted by the elements of Groups II, VI, and VIII of the Periodic Table. The research octane number of the produced isoalkane hydrocarbons is 86–89, and the motor octane number is 84–86. The compounding of the fractions of alkylation gasoline and reformat gasoline that are synthesized in the catalytic reactors allows for high-octane gasolines of various grades to be produced.

NOTATION

- \mathbf{c} —vector of reactant concentrations, mol/l;
- c_{gi} —concentration of the i th reactant in the gas phase, mol/l;
- \mathbf{c}_s —vector of reactant concentrations in the grain of the catalyst, mol/l;
- c_{li} —concentration of the i th reactant in the inner zone of the granule of the catalyst, mol/l;
- c_{oi} —concentration of the i th reactant in the outer zone of the granule of the catalyst, mol/l;
- C_{pg} —heat capacity of the reaction mixture, J/(kg K);
- D_a —axial dispersion coefficient, m^2/s ;
- D_r —radial dispersion coefficient, m^2/s ;
- D_{eff} —effective diffusion coefficient of the i th substance, m^2/s ;
- k_{gi} —mass transfer coefficient of the i th reactant, m/s ;
- K_i —equilibrium constant of the i th stage;

k_{+i} —rate constant of the forward reaction of the i th stage;

k_{-i} —rate constant of the reverse reaction of the i th stage;

l —current length of the reactor, m;

L —length of the catalytic bed, m;

n_{gi} —molar flux of the i th reactant in the gas phase, mol/s;

n_1, n_2, n_3, n_4 —auxiliary variables in the kinetic model of the reaction of methanol synthesis;

P —number of the overall route equations;

r_u —rate of the chemical reaction on the u th route, kmol/(m³s);

r —current radius of the catalytic reactor, m;

r_0 —radius of the inner surface of the radial section of the reactor, m;

R —radius of the outer surface of the radial section of the reactor, m;

\tilde{r} —radius of the inner cylindrical surface of the Raschig ring, m;

\tilde{r}_1 —current radius of the cylindrical Raschig ring, m;

\tilde{R} —radius of the outer cylindrical surface of the Raschig ring, m;

$R_i^B(c, T)$ —rate of the variation of the concentration of the i th substance, kmol/(m³s);

S_{gs} —specific area of the gas–solid interface, m²/m³;

S_r —cross-sectional area of the reactor, m²;

T —temperature in the reactor, K;

T_g —temperature of the gas phase, K;

T_s —temperature of the outer surface of the grain of the catalyst, K;

u_g —linear flow velocity, m/s;

W_i —rate of the i th elementary chemical reaction, kmol/(m³s);

X_i — i th chemical reactant;

α —heat transfer coefficient from the gas stream to the wall of the reactor, W/(m²K);

η_i —efficiency factor of the i th substance;

η_u —efficiency factor of the u th route reaction;

$[\eta]$ —diagonal matrix of the efficiency factors of the reactions that correspond to the overall route equations;

λ_a —thermal conductivity of the mobile phase along the axis of the catalytic zone, W/(m K);

λ_{aef} —effective axial thermal conductivity of the catalyst bed, W/(m K);

λ_{ref} —effective radial thermal conductivity of the catalyst bed, W/(m K);

ΔH_u —thermal effect of the u th overall route reaction, J/kmol;

ρ —current radius of the grain of the catalyst, m;

ρ_B —density of the catalyst, kg/m³;

ρ_g —density of the reaction mixture, kg/m³.

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